

Fast Ewald Sums for General van der Waals Potentials

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ABSTRACT: This work considers ways to increase calculation speed for Ewald crystal summations in cases where standard combination rules do not apply. This also increases speed of free-energy perturbation theory calculations.
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Introduction

For molecular dynamics (MD) simulations of infinite crystals, accurate and efficient calculation of long-range nonbond interactions (Coulomb and London dispersion) is essential.¹

Computation effort can be decreased by using cutoffs in the lattice sums,^{1,2} however, this comes at the expense of considerable decrease in accuracy.³ The method of choice for combining accuracy and cost has been the Ewald method in which some of the interactions are summed in real space and the others in reciprocal space (Fourier transforms).^{4,5}

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We will consider here some improvements in the reciprocal space part of lattice sums for London dispersion terms.

Review of Ewald for London Dispersion

Consider the lattice sum for the London dispersion terms:

$$V_6^{vdw} = -\frac{1}{2} \sum_{L,j} \frac{A_{ij}}{|\mathbf{r}_i - \mathbf{r}_j - \mathbf{R}_L|^6} \quad (1)$$

where \mathbf{r}_i and \mathbf{r}_j are the coordinates of atoms i and j in the unit cell and \mathbf{R}_L is the lattice translation vector. The sums over i and j each go over all atoms inside the cell, except that $i \neq j$ when $L = 0$. Using Ewald procedures this can be rewritten as^{4,5}:

$$V_6^{vdw} = V_{6x}^{vdw} + V_{6h}^{vdw} + V_{60}^{vdw} \quad (2)$$

The real space sum is:

$$-V_{6x}^{v dw} = \frac{1}{\eta^6} \sum_L \left[\sum_{j>i} A_{ij} a^{-2} e^{-a^2} \left(a^{-4} + a^{-2} + \frac{1}{2} \right) + \frac{1}{2} a_L^{-2} e^{-a_L^2} \left(a_L^{-4} + a_L^{-2} + \frac{1}{2} \right) \sum_i A_{ii} \right] \quad (3)$$

where:

$$a = \frac{|\mathbf{r}_i - \mathbf{r}_j - \mathbf{R}_L|}{\eta} \quad (4)$$

$$a_L = \frac{|\mathbf{R}_L|}{\eta} \quad (5)$$

and η is the convergence parameter. The reciprocal space sum is:

$$-V_{6h}^{v dw} = \frac{\pi^{3/2}}{24\Omega} \sum_h' h^3 \left[\pi^{1/2} \text{erfc}(b) + \left(\frac{1}{2b^3} - \frac{1}{b} \right) e^{-b^2} \right] \times \sum_{ij} A_{ij} \cos[\mathbf{h} \cdot (\mathbf{r}_i - \mathbf{r}_j)] \quad (6)$$

where the prime indicates that $\mathbf{h} = 0$ is excluded from the sum and:

$$b = \frac{h\eta}{2} \quad (7)$$

$$h = |\mathbf{h}| \quad (8)$$

The constant:

$$-V_{60}^{v dw} = \frac{\pi^{3/2}}{6\Omega\eta^3} \sum_{ij} A_{ij} - \frac{1}{12\eta^6} \sum_i A_{ii} \quad (9)$$

arises from the $\mathbf{h} = 0$ term.

Assuming that the lattice parameters are ordered as $a < b, c$ with reciprocal lattice vectors satisfying $h_c < h_a, h_b$, the optimum η can be approximated as⁵:

$$\eta^2 = \frac{\Omega}{\pi B \sin \gamma} \quad (10)$$

where Ω is the volume of the unit cell and α, β , and γ are the cell angles.

Karasawa and Goddard⁵ developed accuracy-bounded convergence acceleration (ABCA) criteria for choosing cutoffs R_{cut} and H_{cut} for the lattice

sum in $V_{6x}^{v dw}$ and $V_{6h}^{v dw}$, respectively, consistent with a specified level of accuracy. This also leads to improved estimates for η in place of eq. (10).

For ABCA the overall scaling with size is $O(N^{1.5})$, where N is the number of atoms per unit cell. For a fixed real space cutoff the effort in calculating $V_{6x}^{v dw}$ would scale linearly with the size. However, larger N leads to larger unit cells, and the lowest total calculation cost in doing both V_x and V_k leads to an optimum η and cutoffs such that the net scaling is $N^{1.5}$.⁶

Reduction of Pair Form

Calculation of $V_{6h}^{v dw}$ requires evaluation of:

$$\begin{aligned} S(\mathbf{h}) &= \sum_{i,j} A_{ij} \cos[\mathbf{h} \cdot (\mathbf{r}_j - \mathbf{r}_i)] \\ &= \frac{1}{2} \sum_{i,j} A_{ij} [e^{i\mathbf{h} \cdot (\mathbf{r}_j - \mathbf{r}_i)} + e^{-i\mathbf{h} \cdot (\mathbf{r}_j - \mathbf{r}_i)}] \\ &= \sum_{i,j} A_{ij} e^{i\mathbf{h} \cdot (\mathbf{r}_j - \mathbf{r}_i)} \end{aligned} \quad (11)$$

This leads to N^2 calculations of the cosine function, which dominates the calculations.

GEOMETRIC MEAN CASE

If the dispersion terms satisfy the geometric combination rule:

$$A_{ij} = (B_i B_j)^{1/2} \quad (12)$$

we can write eq. (11) as:

$$\begin{aligned} S(\mathbf{h}) &= \sum_{i,j} B_i B_j \exp(-i\mathbf{h} \cdot \mathbf{r}_i) \exp(i\mathbf{h} \cdot \mathbf{r}_j) \\ &= \left[\sum_i B_i \exp(-i\mathbf{h} \cdot \mathbf{r}_i) \right] \left[\sum_j B_j \exp(i\mathbf{h} \cdot \mathbf{r}_j) \right] \\ &= Z_B(\mathbf{h}) Z_B^*(\mathbf{h}) \end{aligned} \quad (13)$$

where:

$$Z_B(h) = \sum_i B_i \exp(-i\mathbf{h} \cdot \mathbf{r}_i) \quad (14)$$

This can be written as⁷:

$$S(\mathbf{h}) = \left[\sum_i B_i \cos(\mathbf{h} \cdot \mathbf{r}_i) \right]^2 + \left[\sum_i B_i \sin(\mathbf{h} \cdot \mathbf{r}_i) \right]^2 \quad (15)$$

so that the calculation effort scales linearly with N .

The impact of this reduction (15) of the pure form (11) is shown in Table I and Figure 1. Here the *slow* case uses (11) and the fast case uses (15). As expected, the fast case is linear in size whereas the slow case is quadratic. Thus, for the 1500-atom case ($5 \times 5 \times 5$ cells) the calculation is speeded up by a *factor* of 175 ($\sim N/9$) by using (15) rather than (11).

GENERAL CASE

For systems which do *not* satisfy the geometric combination rule, we group together all atoms of the same character (same FF parameters) into sets I and write:

$$S(\mathbf{h}) = \sum_{i,j} A_{ij} e^{i\mathbf{h} \cdot (\mathbf{r}_j - \mathbf{r}_i)} = \sum_{I,J} A_{IJ} \sum_{\substack{i \in I \\ j \in J}} e^{i\mathbf{h} \cdot \mathbf{r}_j} e^{-i\mathbf{h} \cdot \mathbf{r}_i}$$

$$= \sum_{I,J} A_{IJ} S_I(\mathbf{h}) S_J(-\mathbf{h}) \quad (16)$$

where:

$$S_J(\mathbf{h}) = \sum_{j \in J} e^{i\mathbf{h} \cdot \mathbf{r}_j} \quad (17)$$

has the sum over all atoms of the same character. This leads to *fast* times with costs that scale linearly with N even for systems that do *not* satisfy the geometric mean rule.

ARITHMETIC MEAN CASE

Some force fields use a geometric mean combination rule for well depths:

$$D_{ij}^0 = D_i D_j \quad (18)$$

but an arithmetic mean combination rule for bond distances:

$$R_{ij}^0 = (\sigma_i + \sigma_j) \quad (19)$$

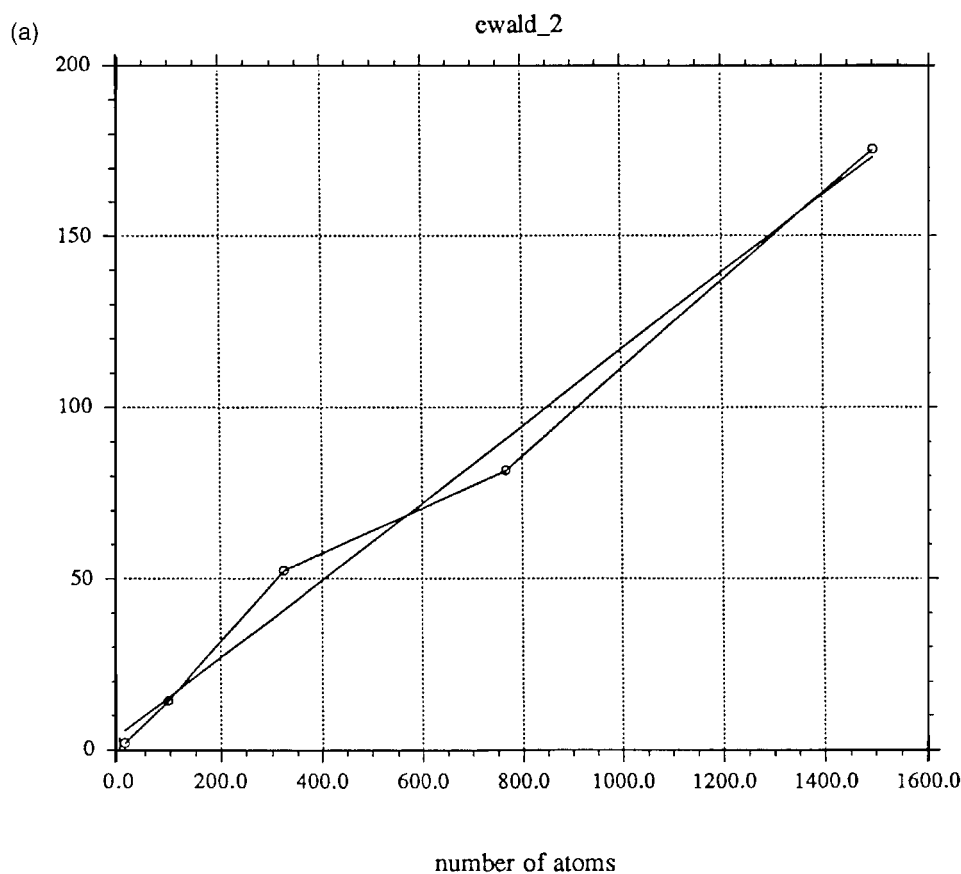


FIGURE 1. (a) The computational time (seconds) per atom for V_{6h}^{vdw} . Here we consider the fast form (circles), eq. (15), versus the slow form (triangles), eq. (11).

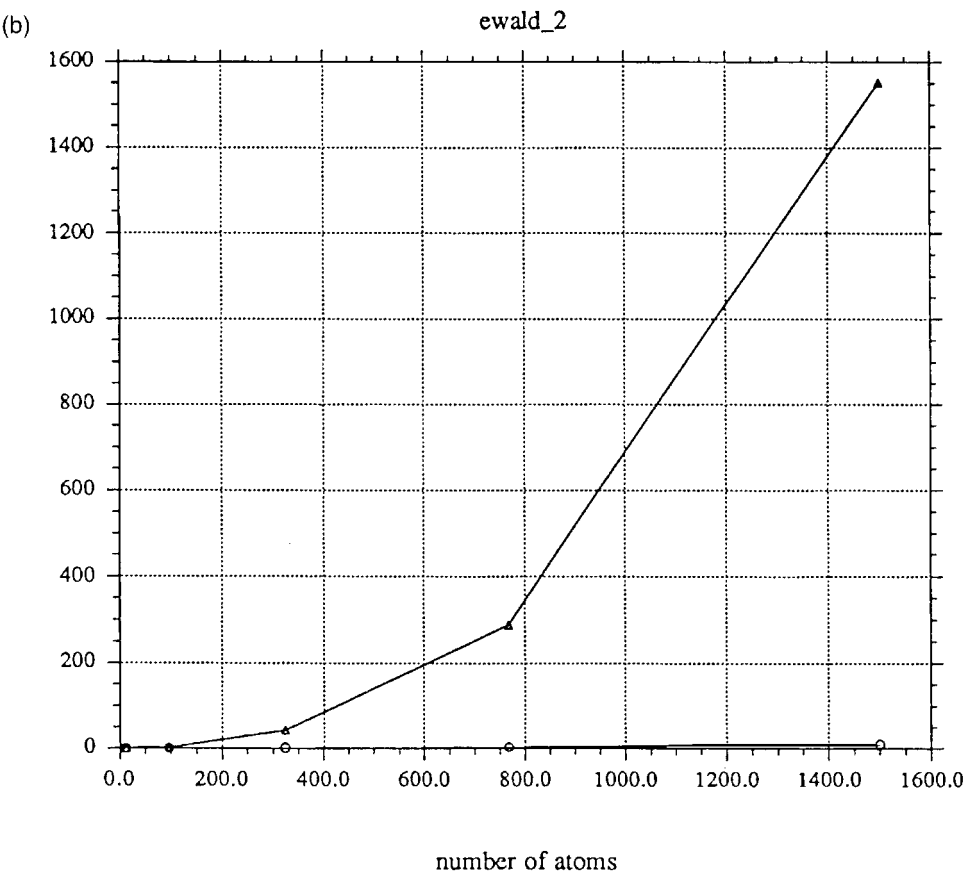


FIGURE 1. (b) The relative time for the fast versus slow calculation. The times are for the SGI 4D/35 workstation. (—○—) Ratio; (—●—) Tfast; (—△—) Tslow.

TABLE I. Accuracy and Cost of Ewald Calculations As a Function of System Size.^a

Supercell	Atoms per Cell	Coulomb						van der Waals–London					
		Ewald Parameters			Error per Atom	Cost		Ewald Parameters			Error per Atom	Cost	
		η	R_{cut}	H_{cut}		V_x^{q+vdw}	V_k^q	η	R_{cut}	H_{cut}		$V_{k,fast}^{vdw}$	$V_{k,slow}^{vdw}$
1 × 1 × 1	12	1.635	4.626	0.696	1.0–3	0.02	0.02	1.818	5.033	0.655	1.0–3	0.01	0.02
2 × 2 × 2	96	2.289	6.728	0.518	1.0–3	0.50	0.26	2.625	6.777	0.438	1.0–3	0.14	2.00
3 × 3 × 3	324	2.799	8.407	0.434	1.0–3	2.68	1.58	3.230	8.407	0.434	1.0–3	0.81	42.45
4 × 4 × 4	768	3.221	9.817	0.382	1.0–3	11.39	8.26	3.784	9.024	0.292	1.0–3	3.53	288.53
5 × 5 × 5	1500	3.624	11.179	0.343	1.0–3	30.86	22.17	4.313	9.971	0.252	1.0–3	8.84	1551.8

^a The test system is polyethylene with the standard unit cell with 12 atoms ($a = 7.2021$, $b = 2.5457$, $c = 4.7953$, $\alpha = \beta = \gamma = 90^\circ$). Here the values of η , R_{cut} , and H_{cut} are from the ABCA values of ref. 6. The computational cost for the real space sums, V_x^q and V_x^{vdw} , have been combined into V_x^{q+vdw} . Note that the computational costs for V_x^{q+vdw} are approximately equal to the time for $V_k^q + V_{k,fast}^{vdw}$. This arises from the use of the ABCA choice of parameters (ref. 5).

For a Lennard–Jones 12-6 potential:

$$V_{ij}^{LJ12-6}(R) = D_{ij}^0 \left[\left(\frac{R_{ij}^0}{R} \right)^{12} - 2 \left(\frac{R_{ij}^0}{R} \right)^6 \right] \\ = F_{ij} R^{-12} - A_{ij} R^{-6}$$

this leads to:

$$F_{ij} = D_{ij}^0 (R_{ij}^0)^{12} \\ A_{ij} = 2 D_{ij}^0 (R_{ij}^0)^6$$

Hence:

$$A_{ij}^{arith} = 2 D_i D_j (\sigma_i + \sigma_j)^6 = 2 \sum_{l=0}^6 P_l D_i D_j \sigma_i^l \sigma_j^{(6-l)} \quad (20)$$

where P_l 's are the Pascal triangle coefficients.

Although (20) does not satisfy (12), it contains seven product terms, thus allowing considerable simplification in evaluating (11). Thus:

$$S^{arith}(\mathbf{h}) = \sum_i \sum_j A_{ij}^{arith} \exp[i\mathbf{h} \cdot (\mathbf{r}_j - \mathbf{r}_i)] \\ = 2 \sum_i \sum_j \sum_{l=0}^6 P_l D_i D_j \sigma_i^l \sigma_j^{(6-l)} \\ \times \exp[i\mathbf{h} \cdot (\mathbf{r}_j - \mathbf{r}_i)] \\ = 2 \sum_{l=0}^6 P_l \left[\sum_i D_i \sigma_i^l \exp(-i\mathbf{h} \cdot \mathbf{r}_i) \right. \\ \left. \times \left(\sum_j D_j \sigma_j^{(6-l)} \exp(i\mathbf{h} \cdot \mathbf{r}_j) \right) \right] \\ = 2 \sum_{l=0}^6 P_l Z_l(\mathbf{h}) Z_{6-l}(-\mathbf{h}) \quad (21)$$

where:

$$Z_l(\mathbf{h}) = \sum_i D_i \sigma_i^l \exp(-i\mathbf{h} \cdot \mathbf{r}_i) \quad (22)$$

Because $P_l = P_{6-l}$, the imaginary parts in (21) cancel, and hence $S(\mathbf{h})$ is real even though the factors in (21) are not equivalent.

Using (21) leads to an $O(7N)$ effort to evaluate $S(\mathbf{h})$ rather than $O(N^2)$ of (11). However, (16) should generally be preferable.

FREE ENERGY PERTURBATION THEORY

In the case of free energy perturbation theory (FEP),⁸ even the Coulomb terms lead to a problem with $S(\mathbf{h})$. In this case the Coulomb interactions between particles i and j are represented by:

$$U_{FEP}(r_{ij}) = \frac{1}{2} \frac{Q_i Q_j}{r_{ij}} \quad (23)$$

where:

$$Q_i = (1 - \lambda)(QA)_i + \lambda(QB)_i \quad (24)$$

Thus, none of the coefficients directly satisfies the geometric combination rule (12), and the reduction in (13) cannot be applied. However, (24) with (23) leads to:

$$Q_i Q_j = (1 - \lambda)^2 (QA)_i (QA)_j \\ + (1 - \lambda) \lambda (QA)_i (QB)_j \\ + (1 - \lambda) \lambda (QA)_j (QB)_i \\ + (1 - \lambda)^2 (QB)_i (QB)_j \quad (25)$$

Thus in (25) we have four terms each of which has the indexes i and j factored and satisfying the generalized combination rule. Thus

$$S^{FEP}(\mathbf{h}) = \sum_i \sum_j A_{ij}^{FEP} \exp[i\mathbf{h} \cdot (\mathbf{r}_j - \mathbf{r}_i)] \\ = (1 - \lambda)^2 [Z_A(\mathbf{h}) Z_A(-\mathbf{h}) \\ + Z_B(\mathbf{h}) Z_B(-\mathbf{h})] \\ + (1 - \lambda) \lambda [Z_A(\mathbf{h}) Z_B(-\mathbf{h}) \\ + Z_B(\mathbf{h}) Z_A(-\mathbf{h})] \quad (26)$$

where:

$$Z_A(\mathbf{h}) = \sum_i (QA)_i \exp(-i\mathbf{h} \cdot \mathbf{r}_i) \quad (27)$$

$$Z_B(\mathbf{h}) = \sum_i (QB)_i \exp(-i\mathbf{h} \cdot \mathbf{r}_i) \quad (28)$$

Consequently, the effort in $U_{FEP}(ij)$ can be reduced from $O(N^2)$ for $O(3N)$.

A similar gain is obtained for the van der Waals terms with FEP.

Results and Discussion

The timing tests were carried out with POLYGRAF 3.22 on a SGI 4D/35 workstation.⁹ For these tests we used polyethylene with the Dreiding force field.¹⁰ This involves both van der Waals and Coulomb interactions, providing a realistic assessment of the impact of these methods.

For each case we used Ewald parameters (η, R_{cut}, H_{cut}) determined by the ABCA procedure.⁵ this complicates the relation between CPU times for different-sized systems. However, the dependence of CPU time on the number of atoms can be written as:

$$T_{fast} = C_1 f(n) * (7n) \quad (22)$$

and:

$$T_{slow} = C_2 f(n) * (0.5n^2) \quad (23)$$

leading to:

$$R = \frac{T_{slow}}{T_{fast}} = \frac{C_2}{C_1} \frac{n}{14} = C_3 * n \quad (24)$$

where C_1 , C_2 , and C_3 are independent of the size of system and $f(n)$ is determined solely by ABCA. For PE we find that $C_3 \sim (1/9)$, suggesting that $C_2/C_1 \sim 1.5$.

The test in Figure 1 and Table I is for the dispersion term case; however, similar gains would be achieved for FEP.

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